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Kokai Patent No. Sho 52(1977)-5320

Publication Date: January 17, 1977

International Class:  
D 01 F 6/62

Japanese Class:  
42 D 12

Intrabureau No.:  
7206-47

Request for Examination: Not Requested

(Total of 5 pages)

Number of Inventions: 1

METHOD FOR MANUFACTURING POLYESTER FIBER

Application No.: Sho 50(1975)-80924

Application Date: July 2, 1975

Inventors: Takatoshi Kuratsuji  
1-2-2 Obumachi, Iwakuni-shi, Yamaguchi-ken.

Applicant: Teijin Limited  
1-11 Minimhoncho, Higashi-ku, Osaka-shi

## Specification

### 1. Title of the Invention

#### METHOD FOR MANUFACTURING POLYESTER FIBER

### 2. Claims

1. A polyester fiber which contains terephthalic acid as a main acid component and trimethylene glycol as a main glycol component, wherein the elasticity recovery in the 10% elongation mode is 90% or above, and the work recovery in the 10% elongation mode is 70% or above.

2. A method for manufacturing the polyester fiber specified in Claim 1 with the following characteristics: when a fiber is manufactured by using a polyester which contains terephthalic acid as a main acid component and trimethylene glycol as a main glycol component, said polyester is melt-spun, and after the resulting spun yarn has been collected without cooling said yarn in an asymmetrical fashion, the resulting unstretched yarn is stretched at a temperature of 20°C or above and 80°C or below at a draw ratio corresponding to at least 70% and no more than 99.9% of the maximal stretching draw ratio at said temperature.

### 3. Detailed explanation of the invention

The present invention concerns a polytrimethylene terephthalate fiber as well as its manufacturing method. The foremost objective of the present invention is to provide a polyester fiber which exhibits excellent elasticity recovery and work recovery, which have been impossible to attain by using conventional fibers.

Polyesters, polyamides, and polyetheresters have been utilized extensively as garment synthetic fibers, and said polymers are utilized for various purposes based on their unique characteristics.

Since polyethylene terephthalate (it may be referred to simply as "PET" on later occasions), which is a general-purpose polyester, exhibits excellent chemical and physical properties, it is utilized for various purposes. The dyeing efficiency of said polymer, however, is inferior. Moreover, the durability factors are inferior to those of nylons. Polytrimethylene terephthalate, which is a terephthalate-type polyester (as in the case of PET), exhibits a dyeing efficiency and durability factors (e.g., elasticity recovery, work recovery, etc.) superior to those of PET.

There are conventionally-known polytrimethylene terephthalate fibers (see Japanese Patent Application Publication No. Kokai Sho 49[1974]-21256). Said patent publication notes a case where a filament or staple characterized by an excellent restoring efficiency (i.e., recovery) is manufactured by using a polytrimethylene terephthalate with a melting point of 222.0°C [or] 219.5°C. As for the performances of said fiber, it is simply stated that the tensile restoring efficiency (i.e., elasticity recovery in the 5% elongation mode) is 60% or above and that the work restoring efficiency (i.e., work recovery in the 5% elongation mode) is 30% or above, and no concrete data are provided. As for the procedures for manufacturing said fiber, only one case where an unstretched polytrimethylene terephthalate yarn is stretched in an 82°C bath at a flask of 3.20 is mentioned.

Upon further research, the present inventors have discovered that the polyester fiber obtained in said patent publication fails to exhibit the objective elasticity recovery and work recovery of the present invention. The

present inventors compiled additional research in order to fully exploit the excellent properties of polytrimethylene terephthalate, and as a result, it has been discovered that said fiber is characterized by excellent elasticity recovery and work recovery and that said fiber can be obtained at a special stretching temperature and at a special stretching draw ratio. The present invention has been completed based on these discoveries.

Put succinctly, the present invention concerns (1) a polyester fiber which contains terephthalic acid as a main acid component and trimethylene glycol as a main glycol component, wherein the elasticity recovery in the 10% elongation mode is 90% or above, and the work recovery in the 10% elongation mode is 70% or above and (2) a method for manufacturing the polyester fiber specified in Claim 1 with the following characteristics: when a fiber is manufactured by using a polyester which contains terephthalic acid as a main acid component and trimethylene glycol as a main glycol component, said polyester is melt-spun, and after the resulting spun yarn has been collected without cooling said yarn in an asymmetrical fashion, the resulting unstretched yarn is stretched at a temperature of 20°C or above and 80°C or below at a draw ratio corresponding to at least 70% and no more than 99.9% of the maximal stretching draw ratio at said temperature.

The polyester employed in the present invention is a polyester which contains terephthalic acid as a main acid component and trimethylene glycol as a main glycol component. The main repetition unit is trimethylene terephthalate. As far as the present specification is concerned, the expression "main" signifies a concentration of approximately 70 mol% or above, more preferably 80 mol% or above, or most preferably 90 mol% or below.

In other words, it is also possible to utilize a polytrimethylene terephthalate wherein no more than 30 mol%, more preferably no more than 20 mol%, or most preferably no more than 10 mol%, of other acid components and/or glycol components have been copolymerized.

Concrete examples of copolymerizable third components include (1) aliphatic dicarboxylic acids (e.g., oxalic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, etc.), (2) alicyclic dicarboxylic acids (e.g., cyclobutanedicarboxylic acid, cyclohexanedicarboxylic acid, decalindicarboxylic acid, biscyclohexyldicarboxylic acid, etc.), (3) aromatic dicarboxylic acids (e.g., isophthalic acid, 5-sodiumsulfoisophthalic acid, chloroterephthalic acid, bromoterephthalic acid, dichloroterephthalic acid, dibromoisophthalic acid, naphthalenedicarboxylic acid, tetralindicarboxylic acid, chloronaphthalenedicarboxylic acid, bromonaphthalenedicarboxylic acid, diphenyldicarboxylic acid, diphenyletherdicarboxylic acid, diphenylsulfonedicarboxylic acid, diphenoxyethanedicarboxylic acid, diphenylketonedicarboxylic acid, 1,2,3,4,5,6-hexahydrodiphenyldicarboxylic acid, etc.), (4) aliphatic glycols (e.g., ethylene glycol, propylene glycol (-1,2), tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, octamethylene glycol, decamethylene glycol, neopentylene glycol, etc.), (5) alicyclic glycols (e.g., cyclohexanediol, cyclohexanedimethanol, decalindimethanol, tricyclodecanedimethanol, etc.), (6) aromatic dioxy compounds (e.g., hydroquinone, bisphenol A, 4,4'-dioxybiphenyl, 4,4'-dioxydiphenylsulfone, 1,1-bis(p-oxyphenyl)cyclohexane, etc.), (7) aliphatic nucleus-containing aliphatic glycols (e.g., 1,4-bis(β-hydroxyethoxy)benzene, 2,2-bis(p-β-hydroxyethoxyphenyl)propane, 4,4'-bis(p-β-hydroxyethoxyphenyl)sulfone, 2,2-bis(4-β-hydroxyethoxy-3,5-

dichlorophenyl)propane, 2,2-bis(4-8-hydroxyethoxy-3,5-dibromophenyl)propane, 4,4'-bis(4-8-hydroxyethoxy-3,5-dichlorophenyl)sulfone, 4,4'-bis(4-8-hydroxyethoxy-3,5-dibromophenyl)sulfone, etc.), (8) polyether glycols (e.g., polyethylene glycol, polypropylene glycol, polytrimethylene glycol, polyhexamethylene glycol, etc.), (9) aliphatic oxycarboxylic acids (e.g.,  $\omega$ -oxycaproic acid,  $\omega$ -oxyundecanic acid, etc.), and (10) aromatic oxycarboxylic acids (e.g., p-oxybenzoic acid, p-8-hydroxyethoxybenzoic acid, p-(p-8-hydroxyethoxy)phenylbenzoic acid, etc.). It is also possible to utilize (11) compounds which possess a single ester-forming functional group (e.g., benzoic acid, naphthoic acid, methoxypolyalkylene glycols, etc.) or (12) compounds which possess 3 or more ester-forming functional groups (e.g., glycerin, trimethylolpropane, pentaerythritol, trimellitic acid, trimesic acid, pyromellitic acid, etc.) so long as virtually linear polymers are obtained.

The polyester may also contain delustering agents (e.g., titanium dioxide, etc.), stabilizers (e.g., phosphoric acid, phosphorous acid, phosphonic acid, and their esters), ultraviolet absorbents (e.g., hydroxybenzenetriazole derivatives, hydroxybenzophenone derivatives, cyanoacrylate derivatives, etc.), crystalline nucleating agents (e.g., talc, etc.), lubricants (e.g., aerosil, china clay, etc.), antioxidants (e.g., hindered phenol derivatives, etc.), pigments, fluorescent whiteness enhancers, etc.

The fiber of the present invention is characterized by an elasticity recovery of 90% or above in the 10% elongation mode and a work recovery of 70% or above in the 10% elongation mode. These recovery factors are defined as follows:

Elasticity recovery in the 10% elongation mode (it may be referred to simply as "TR<sub>10</sub>"): after an initial load of 1/80 g has been impressed on each sample, said sample is stretched at a constant rate of 20%/min., and when the elongation has reached 10%, said sample is shrunk at the same rate, and a stress-strain curve is drawn. If the residual elongation at a point where the stress had dropped to 1/80 g/d (i.e., level equal to the initial load) during the shrinking process is defined as  $\epsilon$ , the following equation holds:  $TR_{10} = (10 - \epsilon)/10 \times 100$  (%).

Work recovery in the 10% elongation mode (it may be referred to simply as "WR<sub>10</sub>"): the following equation can be drawn from the stress-strain curve which had been drawn during the measurement of TR<sub>10</sub>:  $WR_{10} = \text{area below the shrinkage curve} / \text{area below the elongation curve} \times 100$  (%). As the foregoing definitions clearly indicate, TR<sub>10</sub> pertains to the extent to which the length is recovered by strain, and WR<sub>10</sub> pertains to the extent to which the energy is recovered in the same process.

As far as conventional synthetic fibers are concerned, nylons and polyetheresters are characterized by high recoveries. The TR<sub>10</sub> of nylon 6 is as high as 90% or above, but the WR<sub>10</sub> is only approximately 50%. The TR<sub>10</sub> and WR<sub>10</sub> of polyethylene p-oxybenzoate are approximately 80% and below 50%, respectively. There are virtually no conventional fibers which can match the excellent recoveries of the present invention (i.e., TR<sub>10</sub> of 90% or above and WR<sub>10</sub> of 70% or above) with the exception of some high-elongation fibers (e.g., Spandex, etc.).

When a polytrimethylene terephthalate fiber which exhibits such properties is manufactured, it is necessary that the spun yarn be collected without cooling said yarn in an asymmetrical fashion and the resulting

unstretched yarn be stretched at a temperature of 20°C or above and 80°C or below at a draw ratio corresponding to at least 70% and no more than 99.9% of the maximal stretching draw ratio at said temperature. If the spun yarn is cooled in an asymmetrical fashion, the recoveries deteriorate, and the stabilities also deteriorate during the stretching and thermal treatment processes.

If the stretching temperature is lower than 20°C, the stretching tension increases, and as a result, the fracture strength deteriorates. Moreover, the yarn is whitened due to the presence of voids. If the temperature exceeds 80°C, the fiber is stretched without being oriented (i.e., so-called "flow"), and as a result, a heterogeneous fiber is obtained. Especially desirable results are obtained if the stretching temperature is maintained within a range of 40-75°C. It is necessary that draw ratio be maintained at a level corresponding to at least 70% and no more than 99.9% of the maximal stretching draw ratio at the stretching temperature. If said value is below 70%, the  $TR_{11}$  is 90% or above, but the work recovery (i.e.,  $WR_{11}$ ) is below 70%. In such a case, the durability factors deteriorate due to an energy loss. If said value exceeds 99.9%, it is undesirable since fiber fluffs are produced. Especially desirable results are obtained if said value is controlled within a range of 80-98%.

Generally speaking, garment fibers are stretched at a draw ratio corresponding to 75-80% (approximately 85% at the highest) of the maximal stretching draw ratio. If the draw ratio exceeds 90%, the elongation significantly deteriorates. Even if polytrimethylene terephthalate is stretched at 99% of the maximum, the residual elongation is 25% or above,



which was totally unexpected and which was discovered for the first time by the present inventors as a result of various experiments.

The fiber of the present invention may be thermally treated after the stretching process, if circumstances so dictate.

As the foregoing explanations clearly demonstrate, the present invention provides a high-recovery terephthalate-type polyester (as in the case of PET) which exhibits a dyeing efficiency superior to that of PET and durability factors (e.g., elasticity recovery, work recovery, etc.) superior to those of conventional nylon fibers, etc.

In the paragraphs to follow, the contents of the present invention will be explained in further detail with reference to application examples. In subsequent application examples, the specific viscosity was measured based on the viscosity of an o-chlorophenol polymer solution at 35°C.

Application Examples 1 through 3 and Comparative Examples 1 through 4

After a polytrimethylene terephthalate with a specific viscosity of 0.70 had been melted at 265°C, it was extruded from a nozzle equipped with 12 holes with a diameter of 0.5 mm $\phi$  at a rate of 8 g/min., and the resulting extruded product was collected at a rate of 360 m/min. The resulting unstretched yarn was stretched under the various conditions shown in Table I, and it was thermally treated at the original length at 130°C. As a result, the resulting fibers exhibited the properties shown in the right half of the same table.

The elasticity recoveries and work recoveries of the fibers of the present invention were 90% or above and 70% or above, respectively. The stretching temperature was excessively high in Comparative Example 3. As a result, a partial flow was observed, and since the performance variations were significant, the fiber was unusable for practical purposes.

## Comparative Example 5

Procedures identical to those in Application Example 1 were carried out except that cold air (15°C) was blown in a zone between 10 cm and 80 cm below the spinning nozzle at a pressure difference of 150 mmH<sub>2</sub>O (i.e., pressure equivalent to 150 mm of a water cylinder), and one side of the spun yarn was cooled in an asymmetrical fashion. Otherwise polytrimethylene terephthalate was spun under conditions identical to those in Application Example 1. After the resulting unstretched yarn had been stretched at a temperature of 50°C and at a draw ratio of 8.6, it was thermally treated at 120°C at the original length and then wound. The elasticity recovery (in the 10% elongation mode)

Table 1

	Stretching conditions			Fiber performances			
	Temp. (°C)	Maximal stretching draw ratio (equivalents) (DR <sub>max</sub> )	Stretching draw ratio DR/DR <sub>max</sub>	Strength g/d	Elongation %	TR <sub>10</sub> %	WR <sub>10</sub> %
Application example 1	60	4.6	4.0 (87%)	4.1	27	96	80
" 2	60	4.6	4.4 (96%)	4.6	24	93	78
" 3	35	4.3	3.0 (71%)	2.6	40	90	70
Comparative example 1	15	8.4	8.0 (88%)	2.5	49	78	54
" 2	85	4.8	4.0 (88%)	27-67 (Partial flow and considerable performance variations)	25-40	97-90	80-60
" 3	60	4.6	8.0 (65%)	2.7	51	88	62
" 4	60	4.6	4.6 (100%)	(Winding difficult due to fluffing)			

and the work recovery (in the 10% elongation mode) of the resulting fiber were 85% and 69%, respectively. Thus, the recoveries were somewhat inferior. Moreover, the operative stability was low since fluffing was observed during the stretching and thermal treatment processes.